

# Comment on “Understanding the $\mu$ SR spectra of MnSi without magnetic polarons”

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(Dated: 9 September 2014)

Amato *et al.* have reported transverse field muon spin rotation experiments performed on single crystal of MnSi in a single magnetic field of 5200 Oe at a single temperature of 50 K. They present the angular dependence of the muon precession frequencies which they interpret in terms of dipolar magnetic field experienced by bare muons. Such interpretation comes from a rather mechanistic approach without plausible physical backing: the wealth of experimental data collected so far does not justify this oversimplification. No consideration is given to a fundamental feature of MnSi — strong magnetic field inhomogeneities on the scale of a lattice spacing found by many different techniques. The computational procedure also raises a number of objections, in particular, applicability of Kohn-Sham DFT to strongly correlated systems like MnSi. We demonstrate that the conclusion of “Understanding the  $\mu$ SR spectra of MnSi without magnetic polarons” is premature.

PACS numbers: 71.38.Ht, 71.70.Gm, 72.80.Ga, 76.75.+i

Recently, new muon spin rotation ( $\mu$ SR) measurements and associated calculations have been reported in the strongly correlated electron (SCE) system MnSi [1]. The authors of Ref. [1] claim that their work provides understanding of  $\mu$ SR spectra of MnSi without invoking magnetic polarons. Indeed, there is a controversy concerning the origin of several frequencies in the  $\mu$ SR spectra. The conventional approach is to ascribe them to magnetically inequivalent muon stopping sites. It typically assumes that muons stay bare. An alternative reasoning is based on high transverse field  $\mu$ SR experiments demonstrating two-frequency spectra for the wide temperature range 2–305 K and magnetic fields up to 7 T. The spectra are explained by formation of spin (magnetic) polaron (SP) [2] — a few-body state formed by a localized electron mediating ferromagnetic interaction between magnetic ions in its immediate environment.

Amato *et al.* state that such electron localization is impossible in metals, referring to a coupled  $\mu^+e^-$  system (muonium, Mu) which does not show up in metals because of screening of Coulomb interactions [1]. However, formation of SP is an established phenomenon which is widely discussed in SCE metals (see *e.g.* [3–5]). A possible reason for the misleading interpretation of SP as Mu is that both bound states are characterized by certain hyperfine couplings. However, one has to realize the fundamental difference between Mu atom and spin polaron. Muonium is formed in non-magnetic semiconductors and insulators entirely due to the Coulomb interaction between the  $\mu^+$  and the  $e^-$ , characterized by a two-line  $\mu$ SR spin precession spectrum [6] reflecting the electron-muon hyperfine interaction [7]. In contrast, the basic interaction which causes SP formation is the exchange interaction ( $J \sim 1$  eV) between a free carrier and local spins of the magnetic ions of the host, inducing electron

localization into a ferromagnetic (FM) “droplet” on the scale of the lattice spacing [8]. Thermodynamic responses of Mu and SP bound states — dependences on magnetic field and temperature — are also fundamentally different. Mu *cannot* be observed when its electron wavefunction overlaps with paramagnetic moments: the strong pair exchange interaction of the bound electron with the host’s spins (so-called “spin exchange” [7]) would result in extremely rapid spin fluctuations averaging the hyperfine interaction to zero. In contrast, local ferromagnetic ordering mediated by the trapped SP electron holds the spin “fixed” and results in a non-zero hyperfine interaction. The mere observation of hyperfine-split lines in the  $\mu$ SR spectra in a metal or in a magnetic material is a strong evidence for SP formation.

Here one has to make a clear difference between SP and bound spin polaron (BSP) typically detected in magnetic semiconductors, in particular, *dilute* magnetic semiconductors (DMS, systems like CdMnTe or CdMnSe). The formalism of DMS in terms of BSP is justified by the low concentration of magnetic ions which makes the exchange interaction small compared to the Coulomb interaction. In SCE metals, in particular MnSi, magnetic ions are present in high concentration in every unit cell, which justifies the dominant role of the exchange interaction. Moreover, the current case deals with *free, mobile* SP [3, 4], as opposed to BSP in DMS. The clear difference between free SP and BSP is that the former is spin-saturated while the latter is not. This difference is a direct consequence of the exchange-driven nature of the former versus the Coulomb-dominated origin of the latter. The BSP model (a large species of the scale of many lattice constants) is hardly relevant to the current case as the former is based on the concepts of (light) electron effective mass and (high) dielectric constant, both of which break down in the case of the SP in MnSi — a *small* species with a characteristic radius on the order of a lattice constant which exhibits strong mass *enhancement* reported by various experiments on strongly correlated

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electron materials including MnSi.

In SCE metals SP do form (unlike Mu and BSP) and are detected : as is the case for the more common lattice polaron, formation of a spin polaron may profoundly renormalize the bare electron band (bandwidth  $\Delta_0 \sim 1 - 10$  eV) into a much narrower ( $\Delta_{SP}/k_B \sim 10^{-4} - 10^{-3}$  eV) spin polaron band [3, 9]. Such SP band supports coherent SP dynamics [3]. The band nature of the SP observed is evidenced by the equal amplitudes of SP lines in  $\mu$ SR spectra over the entire temperature range of their existence [2, 5, 10]. As the exchange term in MnSi is the dominant interaction leading to SP formation (the Coulomb interaction is effectively screened), the role of the muon is reduced to that of a “trapping center”: the host lattice is populated by free (mobile) SP [3], one of which is captured by the muon, from which we detect two-frequency Mu-like spectra characteristic of a bound electron state, as in another SCE metal  $\text{Cd}_2\text{Re}_2\text{O}_7$  [5].

This scenario of muon-captured SP necessarily requires pure enough samples with long enough SP mean free pass so that residual defects and impurities do not affect the capture similar to electron capture by the muon in pure insulators and semiconductors to form Mu atom [11–14]. If the capture cross section for such defects and/or impurities is higher than that for the muon, they prevent SP capture by the muon, which in this case stays bare. This is similar to what is observed in impure insulators and semiconductors which exhibit no or severely reduced Mu formation probability [13, 15]. Unfortunately, residual resistivity of MnSi sample used in Ref. [1] is not reported to compare with that reported in Ref. [2]. Therefore we do not exclude such a possibility that pure enough samples studied in Ref. [2] reveal SP spectra while the sample measured in Ref. [1] exhibits bare muon state.

In any case, the authors of Ref. [1] do not discuss any physical reasons that can differentiate the two interpretations. Instead, they provide a rather mechanistic approach where major features of the spectra are attributed to some local magnetic fields without much regard for their physical origin. The attempt to interpret the spectra should be commended but i) the claimed *understanding* can be reached only when the performed mathematical manipulations correspond to a consistent physical picture; ii) the methodology used raises more questions than provides answers.

First of all, it is necessary to reiterate the major physical reasons behind the spin polaron model of MnSi. When a coupled  $\mu^+e^-$  SP state is formed, muon spin-flip transitions produce a characteristic two-line spectrum in high transverse magnetic field with the splitting being determined by the muon-electron hyperfine interaction [16]. The dependence of the splitting on both magnetic field and temperature in MnSi corresponds well to the SP model [16] with the spin  $S=24\pm 2$  and the Bohr radius of electron  $R \approx 0.4$  nm. This  $R$  sets up the characteristic length scale of the problem — a lattice spacing — also found in several other SCE materials [5, 17–21] The fact

that there is a characteristic dependence of the spectrum on the temperature and the field is totally ignored by the authors of Ref. [1].

In the paramagnetic region, the signal splitting is proportional to the bulk susceptibility. Such behaviour is expected for both spin polaron and bare muon models. In contrast, low-temperature studies can discriminate between the two models.  $\mu$ SR experiments at 25 K [2] show that the splitting increases almost 2 times when the external magnetic field increases from 0.5 T to 5 T (at this temperature all the data correspond to the ferromagnetically aligned MnSi) while magnetization increases 20 % at most [22], which is difficult to explain within the bare muon model which ascribes the splitting to the dipolar field induced by local Mn ions.

Furthermore, the two-line splitting is observed *at the room temperature* in the paramagnetic phase well above  $T_C \approx 30$  K, where fast spin fluctuations reduce any local fields at the bare muon to an average Knight shift from conduction electrons, which is typically 2 to 3 orders of magnitude less than the observed splittings [5, 16]. More fundamentally, the conventional explanation based on multiple bare muon sites should lead to abrupt change of the splitting at  $T_C$  which does not show up in our experiment for a wide range of external magnetic fields [2]. This means that muons do not stay bare in MnSi and, therefore, do not act as local magnetometers. Instead, the fact that the line splitting does not exhibit a dramatic change at  $T_C$  indicates that the local environment around the muon is fundamentally different from the rest of the host, which is consistent with local FM phase within SP similar to what is found in other magnetic materials [18, 23]. This experimental fact alone is capable to dismiss the entire picture of a bare muon in MnSi suggested in [1]. Furthermore, the deviations from the weak itinerant-electron magnetism model as revealed by electron spin resonance studies of MnSi are attributed to spin polarons [24]. A mid-infrared feature in optical conductivity spectra of MnSi is an established fingerprint of a polaron species [25]. Likewise, observation of a non-Fermi-liquid behavior at low temperature and strong electron scattering cross sections reflecting inhomogeneities on a scale of the order of the lattice spacing above 200 K is consistent with SP. Finally and most fundamentally, both microscopic magnetic field inhomogeneities on the scale of the lattice spacing discovered by neutron scattering [26], NMR [27] and  $\mu$ SR [28], and an effective-mass enhancement are also consistent with the lattice-spacing-size SP formation.

The conclusion of Ref. [1] about the multiple muon sites is based on a series of fits of  $\mu$ SR signals by four components with equal amplitudes. The authors attribute them to structurally equivalent muon sites (4a Wyckoff position). To prove this hypothesis they consider the weak angular dependence of the frequencies with respect to rotation of the sample. The symmetry of the 4a Wyckoff position means that the sum of dipolar contributions for the 4 components should be exactly

zero irrespective of the sample rotation angle:

$$\sum_{i=1}^4 B_{dip,i}(\phi) = 0. \quad (1)$$

This condition is not satisfied for the angular-dependent parts of the fitted frequencies and the sum gives some residual field  $B_{res}(\phi)$ . This field is relatively large with the amplitude close to that of one of the fitted signals. Instead of considering the source of the discrepancy the authors of Ref. [1] *arbitrarily* modify all the signal frequencies by subtracting  $B_{res}(\phi)/4$  functions from each of them and calling this correction demagnetization field. It means that the experimental data are put into Procrustean bed of the symmetry of 4a Wyckoff position for *all* values of the sample rotation angle.

The angular part of each signal is then fitted by 3 parameters of the dipolar tensor in the reference frame. The authors of Ref. [1] claim that each signal provides us with the full set of parameters, namely, the parameter  $a_{dip}$  representing dipolar tensors in the reference frame of the crystal and Euler angles  $\theta$  and  $\phi$  corresponding to orientation of the sample with respect to crystallographic axes. This is not true. First, the fitted tensor components are not independent because the modification of the angular dependencies (see above) artificially forced them to satisfy the symmetry conditions:

$$\sum_{i=1}^4 A_{ki}^i = 0. \quad (2)$$

Second, it is common knowledge that an arbitrary rotation of a solid is given by three (not two) Euler angles. Two angles define only the plane of rotation, while the third angle defines the orthogonal axes in the plane (or, alternatively, the direction corresponding to zero rotation angle). It is impossible to find 4 independent parameters from 3 dipolar tensor components  $A_{xx}$ ,  $A_{yy}$  and  $A_{xy}$ . Remarkably, the authors of Ref. [1] have somehow chosen the zero rotation angle direction of the MnSi sample in their experiments corresponding exactly to the best fit of the signals by only two Euler angles. This preknowledge of the third Euler angle certainly needs explanation and makes the whole procedure very questionable. Moreover, our analysis shows that the quality of the fits is not that great to estimate parameters with such high precision (like  $a_{dip}$  determined to be -0.2044(40) mole/emu).

The angular dependence of the fitted frequencies (quite arbitrarily divided into dipolar and demagnetization field contributions) explains only a small part of the deviation of signal from the free muon frequency. This large negative shift is explained in Ref. [1] by the contact field arising due to spin-polarization of the conduction electrons at the muon site. At this high temperature such a large contribution cannot be due to the Knight shift. Again, there is a question of precision: the authors of Ref. [1] claim that in equation

$$\mathbf{B}_{cont} = A_{cont}\chi\mathbf{B}_{ext} \quad (3)$$

$B_{cont}$  is determined with precision 4%,  $\chi=0.030$  emu/mole, but they find  $A_{cont}$  from these data with much higher precision (-0.9276(20) mole/emu).

Even if one accepts the interpretation based on the huge hyperfine contact coupling tensor due to conduction electrons, its transferability between 50 K (paramagnetic phase) and 5 K (helimagnetic phase), defining the analysis of zero-field spectra in Ref. [1], is doubtful. It is established that the density of states near the Fermi level is quite different for magnetically ordered and paramagnetic MnSi [29]. Therefore, the assumption that "no massive changes occur on the Fermi surface when crossing  $T_C$ " which is at the heart of zero-field (low-temperature) data discussion of Ref. [1] is at least questionable and needs substantiation. Without that any correspondence between the calculated and experimentally observed frequency can be rendered coincidental. Another highly questionable approximation in the analysis of the ZF- $\mu$ SR spectrum is that the local magnetization on the muon in Eq. (13) is assumed to be an equally weighted sum of Mn moments within a sphere of one lattice constant radius and neglecting all the rest — definitely not the distance dependence expected for the RKKY interaction.

To support their findings the authors of Ref. [1] performed a quantum-mechanical calculation. Its purpose is not clear. First, the calculation was performed for the ferromagnetic state of MnSi, while all the experiments were made for helimagnetic and paramagnetic phases. Second, the method of calculation is inappropriate for MnSi. Density functional theory (DFT) is a quantum computational method replacing the solution of Schroedinger equation by minimizing an energy functional of one-electron density. The exact form of the functional is not known and different approximations for exchange-correlation part of the density functional are used: local density approximation stemming from the known solution for the homogeneous electron gas as well as GGA and meta-GGA corrections trying to improve the functional by adding contributions from the first and the second derivatives of the density. In practice, standard DFT uses Kohn-Sham approximation where the density matrix is defined as coming from a set of non-interacting one-electron quasiparticles, which corresponds to the one-electron band picture in the case of periodic systems. DFT is known to be a working horse for electronic structure calculations of solids. It provides reliable results for many systems but it is far from being universal. The deficiencies of the standard (based on the Kohn-Sham approximation) DFT method are well publicized and explained on the examples of characteristic failures like potential energy curves of  $\text{H}_2^+$  (delocalization error) and  $\text{H}_2$  (static correlation error) [30]. As a consequence, there are general guidelines defining the classes of problems where the results should be considered with a grain of salt (like weak interactions) and where the method should not be applied at all (like studies of global potential energy surfaces and systems with

strong electron correlations).

MnSi is known to be strongly correlated and exhibiting non-Fermi behaviour, *i.e.* it is exactly a system where the standard (Kohn-Sham) DFT is expected to fail and it indeed fails. DFT calculations of different flavours systematically predict the ground state of MnSi to have magnetic moment on Mn close to  $1 \mu_B$  [31–34], while the experimental value is  $0.4 \mu_B$ . A possible reason for this is known from XAS spectra [33]: MnSi has a mixed-valence ground state with significant on-site electron correlations. Therefore, quite expectedly, the authors of Ref. [1] has got the same wrong ground state with magnetic moment on Mn close to  $1 \mu_B$ . The use of time-consuming full potential approaches and generalized gradient approximations is absolutely irrelevant to the problem because single reference calculations cannot describe systems with essentially non-idempotent density matrices. It is also worth noting that the approach used in Ref. [1] is not capable to find magnetic polarons in MnSi.

It is not clear why the authors do not provide details of calculations of muon embedded into MnSi. Surely, DFT calculations of muon stopping sites are routine and  $2 \times 2 \times 2$  supercell calculations of MnSi with muon are not computationally too demanding. The electrostatic potential minima can be successfully used for determination of electrophilic attacking sites but their application for finding equilibrium muon sites is questionable (especially in combination with the wrong ground state) because muon is not a small charge probe and it can perturb its environment significantly. The mixed-valence character of the ground state indicates that the local magnetic structure can be also affected (although the correct description of this effect is beyond the capabilities of the standard DFT approach used in Ref. [1]).

In summary, the argumentation presented above cast serious doubts upon conclusion of Ref. [1]) that  $\mu$ SR spectra of MnSi can be correctly understood without invoking spin polarons.

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